Supporting information belonging to:

Synthesis and Tunability of Abnormal 1,2,3-Triazolylidene Palladium and Rhodium Complexes

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Content

1. Synthetic procedures for 1b–f

General comments. The triazolium salt **1a** was reported previously.[S1] CH_2Cl_2 was dried by passage through solvent purification columns. All other chemicals are commercially available and were used as received. A Biotage Initiator 2.0 apparatus was used for microwave syntheses. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker spectrometers at room temperature, unless stated otherwise, and were referenced to external $SiMe_4$. Chemical shifts (δ) are given in ppm and coupling constants J in Hz. NMR assignments are based on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of the ETH Zürich (Switzerland). Mass spectra were measured by electrospray ionization (ESI-MS) in MeCN on a Bruker 4.7 BioAPEX II instrument. Infrared spectra were recorded on Bruker tensor 27 using a Golden Gate ATR.

Improved synthesis of phenyl azide.[S2] In a flask containing aniline (3 mL, 32.9 mmol) and MeCN (45mL) at 0°C, *t*BuONO (5.85 mL, 49.2 mmol) were added slowly and the solution was stirred 10 min at 0°C. $TMSN_3$ (5.22 mL, 39.6 mmol) were added dropwise to the solution, which was stirred 3 h at 0°C followed by 48 h at rt After evaporation of MeCN, the residu was purified by silica column chromatography using hexane: Et_3N (99:1) as eluent. A yellow oil was obtained after evaporation of volatiles (2.87 g, 73%). Spectroscopic data are identical to those reported, though some assignments have been re-evaluated.

^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.42-7.34 (m, 2H, H^{ortho}), 7.20-7.15 (m, 1H, H^{para}), 7.07-7.03 (m, 2H, H^{meta}); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ 140.1 (C^{ipso}) 129.9 (C^{ortho}), 125.0 (C^{para}), 119.1 (C^{meta}).

Method A. To a solution of NaN_3 (4 equiv) in H_2O, *t*BuOH was added followed by the alkyl halide (1 equiv). After stirring at rt for 48 h, copper wire (0.8 equiv.), alkyne (1.2 equiv.) and an aqueous solution of $CuSO_4$ (1 M, 0.2 equiv.) were added. The obtained solution was then irradiated in a microwave reactor at 100°C using high absorption. Subsequently, an aqueous solution of NH_4OH was added and the solution was extracted with CH_2Cl_2. The combined organic phases were washed with H_2O and brine and dried over Na_2SO_4 before all volatiles were evaporated under reduced pressure. After dissolution of the residue in acetone, the solution was filtered through Celite and evaporated to dryness to provide the corresponding triazole. A high pressure flask was subsequently charged with this triazole in MeCN and an excess of MeI and was heated to 60°C for the time indicated. After evaporation of MeCN, the residue was purified by precipitation and, if specified, by column chromatography.

Method B. To a solution of phenylazide (1 equiv.) in H_2O and *t*BuOH (1:1), alkyne (1.3 equiv.), sodium ascorbic acid (0.4 equiv.) and $CuSO_4$ (0.2 equiv.) were added. After stirring the reaction during the time indicated, the solution was treated in the same way as described in method A.

Synthesis of 1b. According to method A, NaN_3 (1.58 g, 24.3 mmol) in H_2O (8 mL), *t*BuOH (8 mL), EtI (0.48 mL, 5.9 mmol), freshly condensed butyne (5 mL, 62.3 mmol), copper wire (0.3 g, 4.7 mmol), $CuSO_4$ solution (1 M, 1.2 mL, 1.2 mmol) were reacted in the microwave reactor for 30 min. After purification, 1,4-diethyl triazole was obtained as a pale yellow liquid (0.49 g, 65%). ^{1}H NMR (360 MHz, $CDCl_3$, 298 K): δ 7.24 (s, 1H, H_{trz}), 4.28 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_3), 2.65 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CCH_2CH_3), 1.44 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3), 1.18 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CCH_2CH_3); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 298 K): δ 149.7 (C_{trz}), 119.5 (CH_{trz}), 45.0 (NCH_2CH_3), 19.0 (CCH_2CH_3), 15.5 (NCH_2CH_3), 13.6

($CCH_2\mathit{C}H_3$); Anal. Found (calcd) for $C_6H_{11}N_3$ × 1/25 CH_3COCH_3 (125.17): C 57.64 (57.65), H 8.64 (8.89), N 32.73 (32.96).

1,4-diethyl triazole (1.15 g, 9.2 mmol) dissolved in MeCN (25 mL) and MeI (3.5 mL, 56.2 mmol) was heated in a high-pressure flask to 60 °C during 3 d. After evaporation, the residue was purified by column chromatography with a gradient eluent CH_2Cl_2/Et_2O, CH_2Cl_2/acetone to afford **1b** (2.2 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.16 (s, 1H, H_{trz}), 4.75 (q, $^3J_{HH}$ = 7.3 Hz, 2H, $NC\mathit{H}_2CH_3$), 4.29 (s, 3H, NCH_3), 2.99 (q, $^3J_{HH}$ = 7.5 Hz, 2H, $CC\mathit{H}_2CH_3$), 1.67 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $NCH_2C\mathit{H}_3$), 1.43 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $CCH_2C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 145.9 (C_{trz}), 129.1 (CH_{trz}), 49.9 ($N\mathit{C}H_2CH_3$), 38.8 (NCH_3), 18 ($C\mathit{C}H_2CH_3$), 14.9 ($NCH_2\mathit{C}H_3$), 11.7 ($CCH_2\mathit{C}H_3$); HR-MS (ESI): *m/z* 140.11838 (calc. for $C_7H_{14}N_3^+$ 140.11822).

Synthesis of 1c. According to method A, NaN_3 (1.04 g, 16 mmol) in H_2O (8 mL), *t*BuOH (8 mL), BuI (0.46 mL, 4 mmol), hexyne (0.51 mL, 4.4 mmol), Cu(0) (0.2 g, 3.1 mmol), $CuSO_4$ solution (0.8 mL, 0.8 mmol) were reacted in the microwave reactor for 1.5 h. Purification afforded 1,4-dibutyl triazole as a pale yellow oil (0.46 g, 63%). ^{1}H NMR (360 MHz, $CDCl_3$, 298 K): δ 7.20 (s, 1H, H_{trz}), 4.20 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $NC\mathit{H}_2CH_2CH_2CH_3$), 2.59 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CC\mathit{H}_2CH_2CH_2CH_3$), 1.75 (quint, $^3J_{HH}$ = 7.3 Hz. 2H, $NCH_2C\mathit{H}_2CH_2CH_3$), 1.54 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, $CCH_2C\mathit{H}_2CH_2CH_3$), 1.32-1.18 (m, 4H, $CCH_2CH_2C\mathit{H}_2CH_3$, $NCH_2CH_2C\mathit{H}_2CH_3$), 0.85-0.79 (m, 6H, $CCH_2CH_2CH_2C\mathit{H}_3$, $NCH_2CH_2CH_2C\mathit{H}_3$); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 298 K): δ 148.1 (C_{trz}), 120.4 (CH_{trz}), 49.7 ($N\mathit{C}H_2CH_2CH_2CH_3$), 32.2 ($NCH_2\mathit{C}H_2CH_2CH_3$), 31.5 ($CCH_2\mathit{C}H_2CH_2CH_3$), 25.2 ($C\mathit{C}H_2CH_2CH_2CH_3$), 22.2 ($CCH_2CH_2\mathit{C}H_2CH_3$), 19.6 ($NCH_2CH_2\mathit{C}H_2CH_3$), 13.7 ($CCH_2CH_2CH_2\mathit{C}H_3$), 13.3 ($N\mathit{C}H_2CH_2CH_2\mathit{C}H_3$) ; Anal. Found (calcd) for $C_6H_{11}N_3$ × 0.5 H_2O (181.28): C 62.91 (63.12), H 10.41 (10.59), N 21.70 (22.08).

The triazole (0.98 g, 5.4 mmol) dissolved in MeCN (30 mL) and MeI (1 mL, 16 mmol) was stirred in a high-pressure flask to 60 °C for 2.5 d. All MeCN was evaporated and the residue was three times dissolved in acetone (8 mL) and precipitated with pentane (90 mL). After column chromatography (eluted with CH_2Cl_2 first then with acetone), triazolium salt **1c** was obtained as a yellow oil (1.19 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.0 (s, 1H, H_{trz}), 4.60 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.2 (s, 3H, NCH_3), 2.85 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $CCH_2CH_2CH_2CH_3$), 1.90 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.67 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, $CCH_2CH_2CH_2CH_3$), 1.36 (sext, $^3J_{HH}$ = 7.7 Hz, 2H, $CCH_2CH_2CH_2CH_3$), 1.30 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.87-0.82 (m, 6H, $CCH_2CH_2CH_2CH_3$, $NCH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ 144.4 (C_{trz}), 129 (CH_{trz}), 53.7 ($NCH_2CH_2CH_2CH_3$), 38.8 (NCH_3), 31.1 ($NCH_2CH_2CH_2CH_3$), 28.8 ($CCH_2CH_2CH_2CH_3$), 23.5 ($CCH_2CH_2CH_2CH_3$), 21.9 ($CCH_2CH_2CH_2CH_3$), 19.2 ($NCH_2CH_2CH_2CH_3$), 13.4, 13.2 ($CCH_2CH_2CH_2CH_3$ + $NCH_2CH_2CH_2CH_3$); HR-MS (ESI): *m/z* 196.18096 (calc. for $C_{11}H_{22}N_3^+$ 196.180824.

Synthesis of 1d. According to method A, NaN_3 (1.04 g, 16 mmol) in H_2O (8 mL), *t*BuOH (8 mL), BuI (0.46 mL, 4 mmol), phenylacetylene (0.53 mL, 4.8 mmol), Cu(0) (0.21 g, 3.4 mmol), $CuSO_4$ solution (0.8 mL, 0.8 mmol) were reacted in the microwave reactor for 1.5 h. After purification, 1-butyl-4-phenyl triazole was isolated as a yellow oil (0.55 g, 69%). ^{1}H NMR (360 MHz, $CDCl_3$, 298 K): δ 7.82 (d, $^3J_{HH}$ = 7.3 Hz, 2H, $H^{ortho}{}_{ph}$), 7.74 (s, 1H, H_{trz}), 7.42 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $H^{meta}{}_{ph}$), 7.32 (d, $^3J_{HH}$ = 7.3 Hz, 1H, $H^{para}{}_{ph}$), 4.38 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.92 (quint., $^3J_{HH}$ = 7.4 Hz, 2H, $CCH_2CH_2CH_2CH_3$), 1.38 (sext., $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR (90 MHz, $CDCl_3$, 298 K): δ 147.8 (C_{trz}), 130.8 ($C^{ipso}{}_{ph}$), 128.9 ($C^{meta}{}_{ph}$), 128.1 ($C^{para}{}_{ph}$),

125.8 (C^{orthp}_{ph}), 119.5 (CH_{trz}), 50.2 ($NCH_2CH_2CH_2CH_3$), 32.4 ($NCH_2CH_2CH_2CH_3$), 19.8 ($NCH_2CH_2CH_2CH_3$), 13.6 ($NCH_2CH_2CH_2CH_3$).

This triazole (0.64 g, 3.2 mmol) in MeCN (15 mL) was heated with MeI (1.2 mL, 19.3 mmol) to 60 °C during 3 d. After evaporation, the residue was three times dissolved in $CHCl_3$ (5 mL) and precipitated with Et_2O (90 mL), followed by gradient column chromatography using Et_2O, CH_2Cl_2, and finally acetone as eluents to afford **1d** as a yellow oil (0.70 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.42 (s, 1H, H_{trz}), 7.72-7.70 (m, 2H, H^{ortho}_{ph}), 7.54-7.47 (m, 3H, H^{meta}_{ph}, H^{para}_{ph}), 4.74 (t, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.29 (s, 3H, NCH_3), 2.02 (quint., $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.39 (sext., $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.91 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 142.9 (C_{trz}), 131.9 (C_{ph}), 130.5 (C_{ph}), 129.7, 129.6 (C_{ph} + CH_{trz}), 121.7 (C^{ipso}_{ph}), 54.2 ($NCH_2CH_2CH_2CH_3$), 39.5 (NCH_3), 31.2 ($NCH_2CH_2CH_2CH_3$), 19.4 ($NCH_2CH_2CH_2CH_3$), 13.4 ($NCH_2CH_2CH_2CH_3$); HR-MS (ESI): *m/z* 216.14926 (calc. for $C_{13}H_{18}N_3^+$ 216.14952).

Synthesis of 1e. According to method B, PhN_3 (0.64 g, 5.4 mmol) in H_2O/*t*BuOH (1:1) (20 mL), hexyne (0.74 mL, 6.4 mmol), $CuSO_4$ (0.17 g, 1.1 mmol), sodium ascorbic acid (0.43 g, 2.2 mmol) were added and stirred at rt during 48 h. After purification, 1-phenyl-4-butyl triazole was obtained as a dark yellow oil (0.72 g, 66%). The NMR data differ from those published previously,[S3] and are thus reported here: ^{1}H NMR (360 MHz, $CDCl_3$, 298 K): δ 7.71 (s, 1H, H_{trz}), 7.66 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H^{ortho}_{ph}), 7.45 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H^{meta}_{ph}), 7.36-7.31 (m, 1H, H^{para}_{ph}), 2.74 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.66 (quint., $^3J_{HH}$ = 7.7 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.37 (sext., $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.90 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 298 K): δ 149.1 (C_{trz}), 137.2 (C^{ipso}_{ph}), 129.6 (C^{meta}_{ph}), 128.3 (C^{para}_{ph}), 120.2 (C^{ortho}_{ph}), 118.8 (CH_{trz}), 31.5

($CH_2CH_2CH_2CH_3$), 25.3 ($CH_2CH_2CH_2CH_3$), 22.3 ($CH_2CH_2CH_2CH_3$), 13.8 ($CCH_2CH_2CH_2CH_3$).

After heating of a solution of 1-phenyl-4-butyl triazole (0.71 g, 3.5 mmol) in MeCN (20 mL) and MeI (2 mL, 32.1 mmol) at 60°C for 20 h, all volatiles were removed under reduced pressure. The residue was twice dissolved in CH_2Cl_2 (10 mL) and precipitated with Et_2O (90 mL). The yellow powder was washed with acetone (15 mL). After evaporation of all volatiles **1e** was isolated as analytically pure pale yellow powder (1.0 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 9.55 (s, 1H, H_{trz}), 8.08-8.02 (m, 2H, $H^{ortho}{}_{ph}$), 7.62-7.57 (m, 3H, $H^{meta}{}_{ph}$, $H^{para}{}_{ph}$), 3.07 (t, $^3J_{HH}$ = 7.8 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.86 (quint., $^3J_{HH}$ = 7.8 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.46 (sext., $^3J_{HH}$ = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_3$), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $CH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ 146.3 (C_{trz}), 134.8 ($C^{ipso}{}_{ph}$), 132.0 ($C^{para}{}_{ph}$),130.5 ($C^{meta}{}_{ph}$), 127.6 (CH_{trz}), 121.7 ($C^{ortho}{}_{ph}$), 39.4 NCH_3, 29.4 ($CH_2CH_2CH_2CH_3$), 24.1 ($CH_2CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_2CH_3$), 13.8 ($CCH_2CH_2CH_2CH_3$); Anal. Found (calcd) for $C_{13}H_{18}IN_3$ (343.21): C 45.71 (45.49), H 5.24 (5.29), N 12.13 (12.24).

Synthesis of 1f. According to method B, PhN_3 **1** (0.45 g, 3.8 mmol) in H_2O/*t*BuOH (1:1) (30 mL), phenylacetylene (0.54 mL, 4.9 mmol), $CuSO_4$ (0.13 g, 0.8 mmol), sodium ascorbic acid (0.3 g, 0.4 mmol) were added and stirred at rt during 48 h. After treatment, 1,4-diphenyl triazole was isolated as a pale yellow powder (0.75 g, 89%). Spectroscopic data are in agreement with those published previously.[S2]

In a high-pressure flask, 1,4-diphenyl triazole (1.89 g, 8.6 mmol) dissolved in MeCN (30 mL) and MeI (3.5 mL, 56.2 mmol) was stirred at 60°C during 4 d. After precipitation of an acetone solution with Et_2O, a pale yellow powder was obtained (2.7 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.74 (s, 1H, H_{trz}), 8.16-8.14 (m, 2H, $H^{ortho}{}_{Nph}$), 8.96-8.94 (m, 2H, $H^{ortho}{}_{Cph}$),

7.59-7.56 (m, 3H, H^{meta}_{Nph}, H^{para}_{Nph}), 7.51-7.48 (m, 3H, H^{meta}_{Cph} H^{para}_{Cph}), 4.44 (s, 1H, NCH_3); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 144.1 (C_{trz}), 134.6 (C^{ipso}_{NPh}), 132 (C^{para}_{CPh}), 131.9 (C^{para}_{NPh}), 130.3 (C^{meta}_{NPh}), 130 (C^{ortho}_{CPh}), 129.6 (C^{meta}_{CPh}), 127.2 ($C_{trz}H$), 121.9 (C^{ortho}_{NPh}), 121.3 (C^{ipso}_{Cph}), 40.1 (NCH_3); Anal. Found (calcd) for $C_{15}H_{14}IN_3$ (363.19): C 49.37 (49.60), H 4.02 (3.89), N 11.56 (11.57).

2. Spectroscopic data for 4a at the slow exchange limit

Table S1. ^1H NMR chemical shifts (500 MHz, CD_3CN, 253 K) of the isomers of complex **4a** [a]

	H^{ortho}_{ar}	NCH_2	NCH_3	NCH_2CH_3
52% isomer	8.20 (7.3 Hz)	4.81 (7.3 Hz)	4.04	1.67 (7.3 Hz)
32% isomer	8.00 (6.8 Hz)	5.00 (7.3 Hz)	3.99	1.83 (7.3 Hz)
11% isomer	8.13 (7.3 Hz)	4.75 (7.3 Hz)	4.02	1.64 (7.3 Hz)
5% isomer	7.94 (7.0 Hz)	4.93 (7.3 Hz)	3.98	1.78 (7.3 Hz)

[a] values in ppm, $^3J_{HH}$ values in parentheses; multiplicities for H^{ortho}_{ar} (d), NCH_2 (q), NCH_2CH_3 (t), H^{meta}_{ar} and H^{para}_{ar} appear as a multiplet (7.65–7.47) that could not be resolved for the different isomers.

3. Spectroscopic data for [Rh(triazolylidene)Cl(CO)$_2$] 7b–f

Synthetic aspects. A flask containing complex **6** in CH_2Cl_2 was saturated with gaseous CO by bubbling for 20 min. The volatiles were subsequently evaporated at rt under high vaccuum and the residue was washed with pentane to give complex **7** as a yellowish residue in essentially quantitative yield. The spectroscopic data of **7a** were published previously.[S1]

Spectroscopic data for 7b. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 4.62 (q, $^{3}J_{HH}$ = 7.3 Hz, 2H, NCH_2CH$_3$), 3.99 (s, 3H, NCH$_3$), 2.87 (q, $^{3}J_{HH}$ = 7.6 Hz, 2H, CCH_2CH$_3$), 1.60 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, NCH$_2$CH_3), 1.35 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H, CCH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ 186.8 (d, $^{1}J_{CRh}$ = 53.4 Hz, CO), 184.3 (d, $^{1}J_{CRh}$ = 74.6 Hz, CO), 159.8 (d, $^{1}J_{CRh}$ = 38.8 Hz, C-Rh), 148.2 (d, $^{2}J_{CRh}$ = 2.2 Hz, C$_{trz}$), 51.0 (NCH$_2$CH$_3$), 36.5 (NCH$_3$), 19.3 (CCH$_2$CH$_3$), 15.8 (NCH$_2$$CH_3$), 14.1 (CCH$_2$$CH_3$); IR ($CH_2Cl_2$): 2065 cm^{-1}, 1983 cm^{-1} (ν_{CO}).

Spectroscopic data for 7c. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 4.56 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, NCH_2CH$_2$CH$_2$CH$_3$), 3.98 (s, 1H, NCH$_3$), 2.83 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, CCH_2CH$_2$CH$_2$CH$_3$), 2.06 (quint., $^{3}J_{HH}$ = 7.4 Hz, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.76 (quint., $^{3}J_{HH}$ = 7.8 Hz, 2H, CCH$_2$CH_2CH$_2$CH$_3$), 1.52-1.32 (m, 4H, CCH$_2$CH$_2$CH_2CH$_3$ NCH$_2$CH$_2$CH_2CH$_3$), 1.01-0.95 (m, 6H, CCH$_2$CH$_2$CH$_2$CH_3, NCH$_2$CH$_2$CH$_2$CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ 187.0 (d, $^{1}J_{CRh}$ = 53.4 Hz, CO), 184.4 (d, $^{1}J_{CRh}$ = 74.8 Hz, CO), 160.4 (d, $^{1}J_{CRh}$ = 39.1 Hz, C-Rh), 147.2 (d, $^{2}J_{CRh}$ = 2.8 Hz, C$_{trz}$), 55.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.6 (NCH$_3$), 32.5 (NCH$_2$$CH_2CH_2CH_3$), 31.9 (CCH$_2$$CH_2CH_2CH_3$), 25.7 (C$CH_2CH_2CH_2CH_3$), 23.0 (CCH$_2CH_2$$CH_2CH_3$), 20.2 (NCH$_2CH_2$$CH_2CH_3$), 14.0, 13.9 (CCH$_2CH_2CH_2$$CH_3$, N$CH_2CH_2CH_2$$CH_3$); IR ($CH_2Cl_2$): 2065 cm^{-1}, 1983 cm^{-1} (ν_{CO}).

Spectroscopic data for 7d. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.76-7.71 (m, 2H, H$^{ortho}_{ph}$), 7.59-7.53 (m, 3H, H$^{meta}_{ph}$, H$^{para}_{ph}$), 4.71 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, NCH_2CH$_2$CH$_2$CH$_3$), 4.04 (s, 3H, NCH$_3$), 2.14 (quint., $^{3}J_{HH}$ = 7.4 Hz, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.45 (sext., $^{3}J_{HH}$ = 7.4 Hz, 2H NCH$_2$CH$_2$CH_2CH$_3$), 1.01 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, NCH$_2$CH$_2$CH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ 186.8 (d, $^{1}J_{CRh}$ = 54.2 Hz, CO), 183.9 (d, $^{1}J_{CRh}$ = 75.4 Hz, CO), 161.3 (d, $^{1}J_{CRh}$ = 38.8 Hz, C-Rh), 146.8 (d, $^{2}J_{CRh}$ = 2.2 Hz, C$_{trz}$), 130.8 (C$^{ortho}_{ph}$),

130.5 (C^{para}_{ph}), 129.3 (C^{meta}_{ph}), 127.9 (C^{ipso}_{ph}), 55.1 ($NCH_2CH_2CH_2CH_3$), 37.9 (NCH_3), 32.5 ($NCH_2CH_2CH_2CH_3$), 20.2 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$); IR (CH_2Cl_2): 2065 cm^{-1}, 1983 cm^{-1} (ν_{CO}).

Spectroscopic data for 7e. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.15-8.09 (m, 2H, H^{ortho}_{ph}), 7.58-7.54 (m, 3H, H^{meta}_{ph}, H^{para}_{ph}), 4.12 (s, 3H, NCH_3), 3.00 (t, $^3J_{HH}$ = 7.8 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.84 (quint., $^3J_{HH}$ = 7.8 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.49 (sext., $^3J_{HH}$ = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.01 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $CH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ 186.7 (d, $^1J_{CRh}$ = 54.9 Hz, CO), 183.8 (d, $^1J_{CRh}$ = 75.4 Hz, CO), 161.8 (d, $^1J_{CRh}$ = 39.5 Hz, C-Rh), 148.3 (d, $^2J_{CRh}$ = 1.5 Hz, C_{trz}), 140.2 (C^{ipso}_{ph}), 130.6 (C^{para}_{ph}), 129.6 (C^{meta}_{ph}), 125.2 (C^{ortho}_{ph}), 37.0 (NCH_3), 31.8 ($CH_2CH_2CH_2CH_3$), 25.7 ($CH_2CH_2CH_2CH_3$), 23.1 ($CH_2CH_2CH_2CH_3$), 14.1 ($CH_2CH_2CH_2CH_3$); IR (CH_2Cl_2): 2065 cm^{-1}, 1983 cm^{-1} (ν_{CO}).

Spectroscopic data for 7f: ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.24-8.20 (m, 2H, H^{ortho}_{Nph}), 7.85-7.81 (m, 2H, H^{ortho}_{Cph}), 7.61-7.57(m, 6H, H^{meta}_{Cph}, H^{para}_{Cph}, H^{meta}_{Nph} H^{para}_{Nph}), 4.15 (s, 1H, NCH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ 186.7 (d, $^1J_{CRh}$ = 54.8 Hz, CO), 183.7 (d, $^1J_{CRh}$ = 74.6 Hz, CO), 162.6 (d, $^1J_{CRh}$ = 39.5 Hz, C-Rh), 147.5 (d, $^2J_{CRh}$ = 2.2 Hz, C_{trz}), 140.2 (C^{ipso}_{ph}), 131.1 (C^{ortho}_{ph}), 130.8 (C^{para}_{ph}), 130.7 (C^{meta}_{ph}), 129.6 (C^{ipso}_{ph}), 129.4 (C^{meta}_{ph}), 127.7 (C^{ortho}_{ph}), 125.3, 38.2 (NCH_3); IR (CH_2Cl_2): 2068cm^{-1}, 1988 cm^{-1} (ν_{CO}).

4. Crystallographic supplementary information

Supplementary information for 3a

A pseudo-polymorph of *cis*–**3a** was formed upon crystallization of the complex from CH_2Cl_2 and pentane. This pseudo-polymorph comprises a co-crystallized molecule of CH_2Cl_2. Bond lengths and angles deviate slightly more than 3σ as compared to the solvent-free structure of *cis*–**3a**, though the principle features are identical (*e.g.*, larger I1–Pd1–I2 angle than C1–Pd1–C12, approximate 80° tilting of the N-heterocycle with respect to the palladium coordination plane).

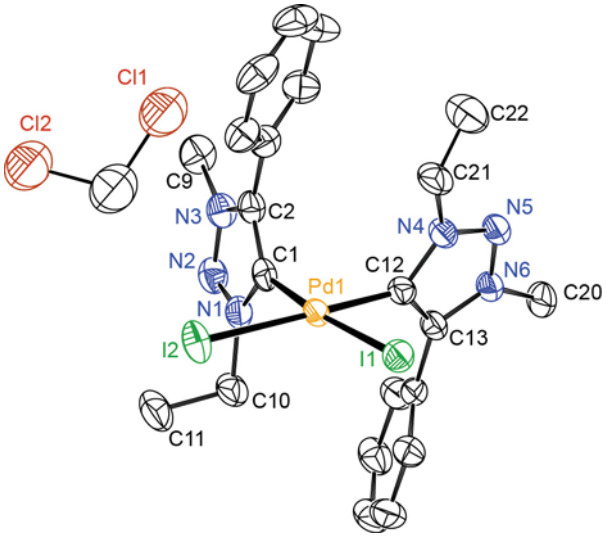

Fig. S1. ORTEP representation of the polymorph *cis*–**3a** × CH_2Cl_2. (50% probability, hydrogens, disorder in the position of the CH_3 group of one ethyl substituent, C22, and in the CH_2Cl_2 molecule omitted for clarity). Selected bond lengths (Å) and angles(°):C1–Pd1 1.992(6), C12–Pd1 1.985(6), I1–Pd1 2.6567(6), I2–Pd1 2.6630(6), C1–Pd1–C12 85.7(2), C1–Pd1–I1 173.39(15), C1–Pd1–I2 90.62(15), C12–Pd1–I1 87.92(17), C12–Pd1–I2 176.08(17), I1–Pd1–I2 95.781(19).

Supplementary information for 5e

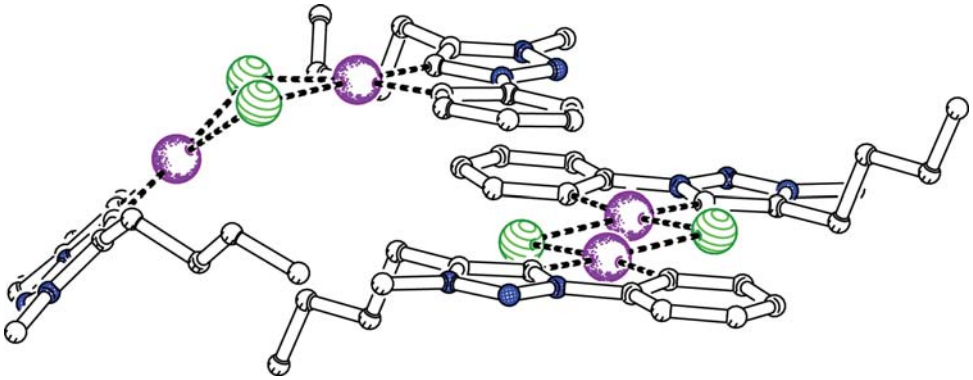

Fig. S2. Illustration of the different geometries of dimeric complexes of **5e**, demonstrating an open-book configuration (top-left; distorted tetrahedral Pd_2I_2 arrangement) and a planar configuration (bottom right, distorted square plane of Pd_2I_2 unit).

Supplementary information for 5f

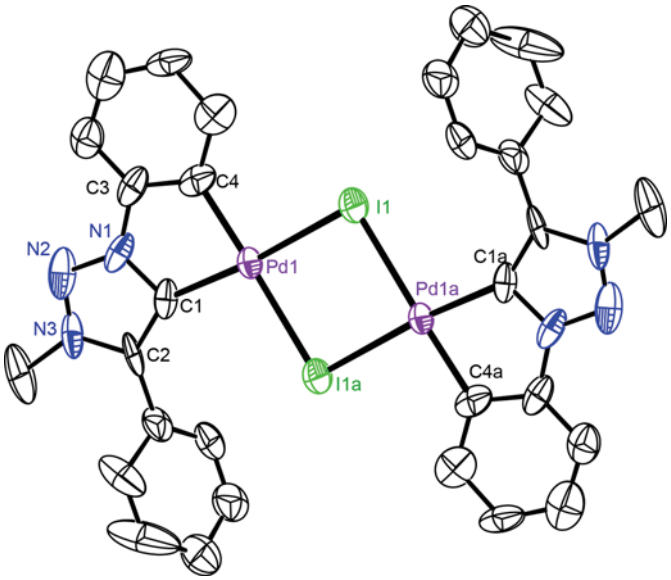

Fig. S3. ORTEP representation of one of the two independent molecules of **5f** comprising a cyclometalated N-phenyl substituent. In both molecules, only the N-bound phenyl group is cyclometalated, no signs for C–H bond activation in the C-bound phenyl substituent were obtained. Both dimeric complexes exhibit an essentially co-planar arrangement of the cyclometalating ligands, the open-book-type distortion is much less pronounced as compared to **5e**.

Structure determination and refinement of the complexes.

Suitable single crystals were mounted on a Stoe Image Plate Diffraction System equipped with a graphite monochromator and data collection was performed using Mo-K_α radiation (λ = 0.71073 Å), except for the crystal of **4a**, which was measured on a SuperNova A diffractometer using Cu-K_α radiation (λ = 1.54184 Å). All structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least-squares on F^2 with SHELXL-97.[S4] All hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL-97 default parameters. All non hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied using MULscanABS for **2a**, **2c**, **2e**, *trans*-**3a**, *cis*-**3a**, and *cis*-**3a** × CH_2Cl_2, and an empirical absorption correction was applied using DELrefABS for **2b**, **2d**, both implemented in PLATON03.[S5] An analytical absorption correction was applied for **4a**.[S6] A numerical absorption correction was applied to **5e** and **5f** using STOE X-Red & X-Shape.[S7]

Complex **2a** crystallized with two independent centrosymmetric binuclear complexes and one disordered molecule of CH_2Cl_2 in the unit cell. One iodide in one molecule is disordered over two positions (occupancy of I3A/I3B is 0.7/0.3). The CH_3 of the ethyl substituents are disordered over two positions in each molecule (occupancies 0.7/0.3). Various restraints were applied, including the phenyl rings in both molecules which were fitted to regular hexagons using the EADP and DFIX instructions. The SQUEEZE routine in PLATON was used to treat disordered solvent.[S5] The potential voids were calculated to contain 115 electrons for a volume of 338.6 $Å^3$ and were attributed to disordered CH_2Cl_2.

The crystal of **2b** was a twin, therefore a twin-integration has been performed taking into account the two parts of the twin. The data set of the major component of the twin has been used for structure solution.

In the crystal of *cis*-**3a** × CH_2Cl_2, the CH_3 group of one ethyl substituent and the CH_2Cl_2 molecule were disordered.

Crystals of **5f** contained volatile solvent and therefore cooling was necessary throughout the mounting procedure in order to afford a sufficiently diffracting specimen. During the refinement, not all solvent molecules could be resolved due to disorder and were thus removed by the SQUEEZE routine in PLATON.[S5] Samples of **5e** showed twinning. Two domains were indexed and integrated using STOE X-Area.[S7] Structure solution and initial refinement was carried out on the basis of non-overlapping reflections, belonging to one domain only. The resulting model was further refined to convergence in SHELXL-97 with a HKLF5 dataset (featuring both domains including overlapping reflections). A free-format CIF using the LIST 6 command was written and imported in WinGX.[S8] Final HKLF4 refinement was carried out. This procedure allows to merge the reflections of the major component and to obtain averaged standard deviations. Further crystallographic details on all complexes are compiled in Table S2.

Table S2. Crystallographic data for all complexes.

	2a	**2b**	**2c**	**2d**	**2e**	*trans*-**3a**	*cis*-**3a**
CCDC number	800720	800721	800722	800724	800723	800725	800726
Color, shape	red block	yellow needle	orange plate	yellow plate	orange plate	yellow rod	pale yellow plate
crystal size/mm	0.16 × 0.22 × 0.45	0.50 × 0.11 × 0.05	0.20 × 0.35 × 0.40	0.20 × 0.18 × 0.13	0.40 × 0.30 × 0.15	0.15 × 0.15 × 0.45	0.15 × 0.15 × 0.10
empirical formula	$C_{22}H_{26}I_4N_6Pd_2$ × 0.5 CH_2Cl_2	$C_{14}H_{26}I_4N_6Pd_2$	$C_{22}H_{42}I_4N_6Pd_2$	$C_{26}H_{34}I_4N_6Pd_2$ × 2 CH_2Cl_2	$C_{26}H_{34}I_4N_6Pd_2$ × CH_2Cl_2	$C_{22}H_{26}I_2N_6Pd$	$C_{22}H_{26}I_2N_6Pd$
Fw	1137.35	998.81	1111.06	1320.84	1235.92	734.69	734.69
T/K	173	173(2)	173	173(2)	173(2)	173	173
cryst syst	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*P*–1 (No. 2)	$P2_1$/n (No. 14)	*P*–1 (No. 2)	*P*–1 (No. 2)	$P2_1$/c (No. 14)	$P2_1$/c (No. 14)	$P2_1$/c (No. 14)
unit cell							
a/Å	11.6395(8)	7.6739(15)	8.2840(8)	9.9204(14)	8.7187(5)	9.6971(7)	9.5874(7)
b/Å	13.1766(10)	14.442(2)	9.6916(9)	10.5994(13)	15.5227(7)	13.6009(12)	13.4276(9)
c/Å	13.3345(9)	11.515(3)	11.8468(11)	10.5337(14)	14.8293(9)	9.4707(8)	19.6702(14)
α/deg	71.430(5)	90	71.804(11)	91.475	90	90	90
β/deg	66.276(5)	92.469(17)	80.644(11)	94.257	96.836(5)	105.490(6)	102.350(8)
γ/deg	70.827(6)	90	69.299(11)	112.019	90	90	90
V/Å^3	1726.9(2)	1275.0(5)	843.77(16)	1022.3(2)	1992.70(19)	1203.71	2473.7(3)
Z	2	2	1	1	8	2	4
D_{calc}/g cm^{-3}	2.106	2.602	2.187	2.146	2.060	2.027	1.973
μ/mm^{-1} (Mo K$_\alpha$)	4.715	6.264	4.745	4.188	4.160	3.357	3.268
no. of total, unique reflns	16880, 6105	9417, 2254	6731, 3090	7810, 3523	25123, 3747	10308, 2268	12387, 4790
R_{int}	0.042	0.2046	0.036	0.1113	0.0316	0.052	0.054
transmn range	0.238–0.475	0.028–0.410	0.205–0.384	0.308–0.576	0.543–0.899	0.3014–0.5997	0.334–0.613
no. paras, restr.	275, 7	70, 0	154, 0	200, 0	199, 0	145, 0	285, 0
R,[a] Rw,[b]	0.0319, 0.0849	0.0836, 0.2110	0.0313, 0.0823	0.0887, 0.2291	0.0291, 0.0972	0.0256, 0.0648	0.0366, 0.0892
GOF	1.02	0.837	0.938	0.996	1.129	0.98	0.91
min/max resid density/e Å^{-3}	-1.00, 0.84	-1.472, 1.068	-1.25, 1.22	-2.569, 1.504	-0.788, 1.373	-0.85, 0.59	-1.65, 0.95

Table S2 (continued). Crystallographic data for complexes.

	cis-**3a** × CH_2Cl_2	**4a**	**5e**	**5f**
CCDC number	800727	800728	800729	800730
Color, shape	yellow needle	yellow block	yellow needle	yellow, block
Crystal size/mm	0.50 × 0.20 × 0.15	0.27 × 0.17 × 0.17	0.5 × 0.2 × 0.07	0.4 × 0.3 × 0.2
Empirical formula	$C_{22}H_{26}I_2N_6Pd \times CH_2Cl_2$	$C_{22}H_{26}Cl_2N_6Pd$	$C_{13}H_{16}IN_3Pd$	$C_{15}H_{12}I_2N_3Pd \times 2/3\ CH_2Cl_2$
Fw /g mol^{-1}	819.61	554.79	447.59	524.19
T/K	173	100	100	100
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	*P*–1 (No. 2)	*P*–1 (No. 2)	$P2_1/n$ (No. 14)
unit cell				
a/Å	12.7461(9)	8.2661(2)	12.4522(11)	15.4702(14)
b/Å	17.2912(9)	8.8875(3)	12.7285(11)	20.6531(10)
c/Å	14.1530(10)	9.3445(3)	15.3977(14)	16.2193(10)
α/deg	90	108.081(3)	73.253(7)	90.00
β/deg	112.592(5)	115.551(3)	66.849(7)	91.153(6)
γ/deg	90	81.735(2)	87.828(7)	90.00
V/$Å^3$	2879.9(3)	577.89(3)	2140.9(3)	5181.1(6)
Z	4	1	6	12
D_{calc}/g cm^{-3}	1.890	1.586	2.083	2.016
μ/mm^{-1} (Mo K_α)	2.997	8.776	3.449	3.067
no. of total, unique reflns	28970, 5134	8246, 2401	42691, 7982	35537, 9049
R_{int}	0.0892	0.0436	n/a[c]	0.1104
Transmission range	0.369–0.520	0.215–0.419	0.182–0.472	0.398–0.644
no. paras, restraints	318, 6	145, 0	493, 0	598, 0
R,[a] *Rw*,[b]	0.0396, 0.0945	0.0421, 0.1139	0.0627, 0.1734	0.0630, 0.1385
GOF	0.91	1.061	1.068	0.949
min/max resid density/e $Å^{-3}$	-1.087, 0.880	–1.618, 1.716	-2.099, 1.117	-1.241, 1.634

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$ for all $I > 2\sigma(I)$; [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$; [c] hklf5 refinement

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